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Recap

Canonical ensemble applications

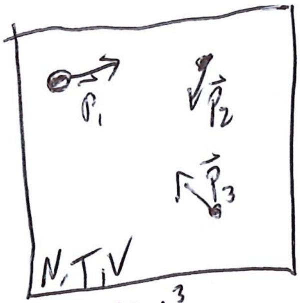
Observable effects from information content

Classical non-rel. ideal gases

Need to regularize to find well-defined partition function

$$Z = \sum_i e^{-\beta E_i}$$

Limit of sums → integrals



$V = L^3$

Declare only possible momenta are

$$\vec{p} = (p_x, p_y, p_z) = \hbar \frac{\pi}{L} (k_x, k_y, k_z) \qquad k_{x,y,z} = 0, 1, 2 \ldots$$

Planck constant converts units ($\frac{1}{L}$ vs. p)

Countable energy levels for each particle

$$E_k = \frac{p^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} k^2 = \varepsilon \left(k_x^2 + k_y^2 + k_z^2\right) \qquad \varepsilon = \frac{\hbar^2 \pi^2}{2mL^2}$$

Lowest energies:

$$\boxed{\frac{E}{\varepsilon} = 0, 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, \ldots}$$

$\vec{k} = (2,1,1)$ + perms.

$\vec{k} = (2,2,0)$ + perms

Not 7, 15, 23, 28, 31, ...

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Unlike spin system, not evenly spaced

First consider single particle $N=1$

$$Z_1 = \sum_i e^{-E_i/T} = \sum_{k_{x,y,z}=0}^{\infty} \exp\left(-\frac{\varepsilon}{T}\left(k_x^2+k_y^2+k_z^2\right)\right)$$

$$= \left(\sum_{k_i=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2}{2mTL^2}k_i^2\right]\right)^3$$

Classical $\rightarrow$ T, L large vs. $\hbar$

Non-rel. $\rightarrow$ m large vs. $\hbar$

$$\left.\begin{matrix} \\ \\ \end{matrix}\right\} \frac{\hbar^2\pi^2}{2mTL^2} \ll 1$$

$k = n \rightarrow n+1$, argument of exp changes by

$$\frac{\hbar^2\pi^2}{2mTL^2}(2n+1)$$

Terms being summed resemble integration unless $n \gg 1$

$n \gg 1$ $\rightarrow$ terms suppressed by $\exp(-n^2)$

Limit of continuous momenta

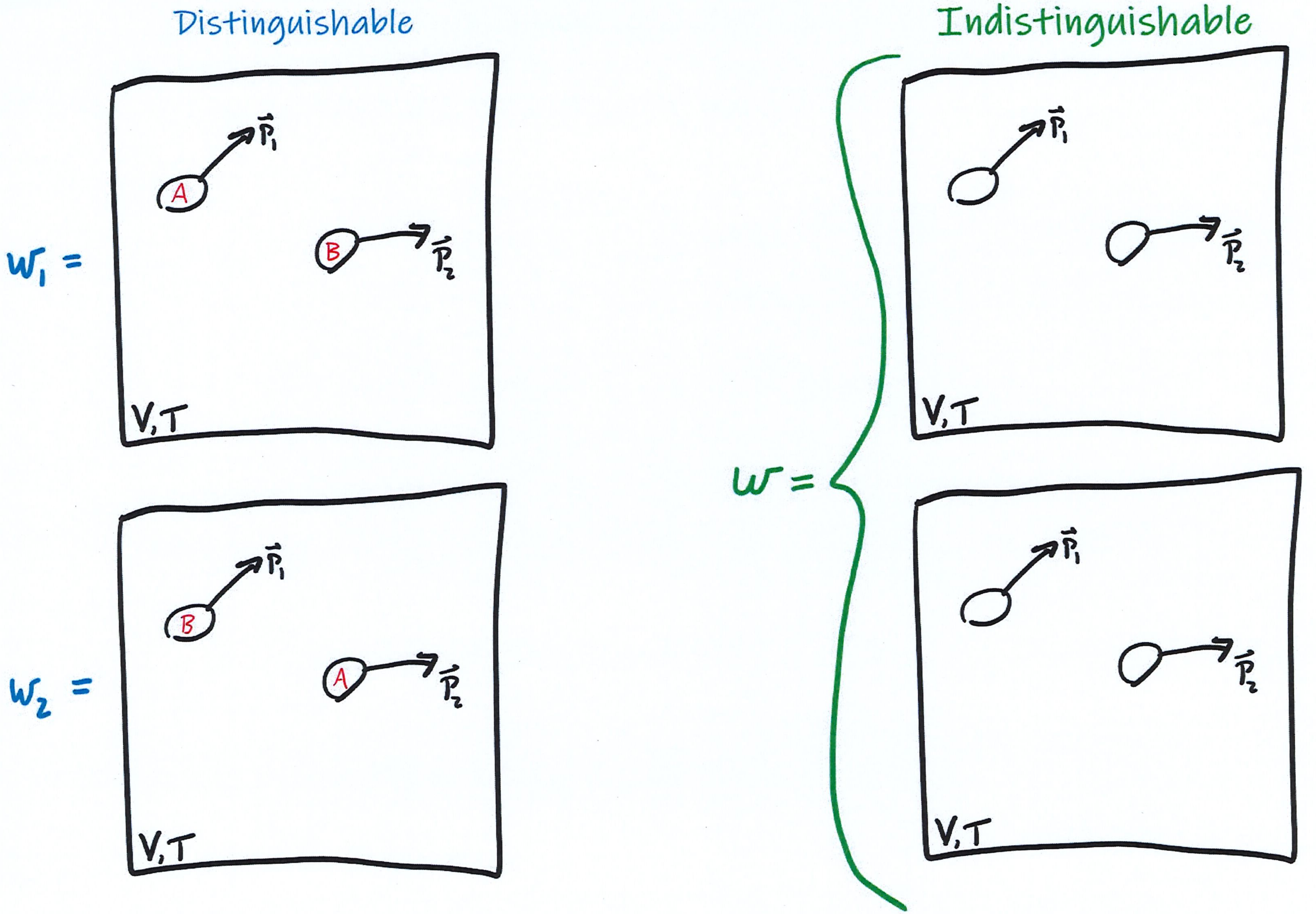
continuous

$$\sum_{k_i=0}^{\infty} \exp\left(-\frac{\varepsilon}{T}k_i^2\right) \rightarrow \int_0^\infty \exp\left(-\frac{\varepsilon}{T}\hat{k}_i^2\right) d\hat{k}_i \qquad p_i = \hbar\frac{\pi}{L}\hat{k}_i$$

$$\cancel{= \int_0^\infty \exp\left(-\frac{\hbar^2\pi^2}{2mTL^2}\left(\hbar\frac{\pi}{L}\right)^2 p^2\right) d\left(\hbar\frac{\pi}{L}p\right)}$$

$$= \int_0^\infty \exp\left(-\frac{\hbar^2\pi^2}{2mTL^2}\left(\frac{L}{\hbar\pi}\right)^2 p_i^2\right) d\left(\frac{Lp_i}{\hbar\pi}\right)$$

$$= \frac{L}{2\hbar\pi}\int_{-\infty}^{\infty} \exp\left(\frac{-p_i^2}{2mT}\right) dp_i$$


Distinguishable
Indistinguishable
W₁ =
W₂ =
W =
V,T
V,T
V,T
V,T
A
B
B
A
p₁
p₂

Generalize to N (distinguishable) particles

$$Z_D = Z_1^N = \left(\frac{L}{2\pi\hbar}\right)^{3N} \int_{-\infty}^{\infty} \exp\left[-\sum_{n=1}^{N} \frac{p_n^2}{2mT}\right] d^{3N}p$$

3N gaussian integrals

$$\left(\sqrt{2\pi mT}\right)^{3N}$$

$$Z_D = \left(\frac{L}{2\pi\hbar}\sqrt{2\pi mT}\right)^{3N} = \left(L\sqrt{\frac{mT}{2\pi\hbar^2}}\right)^{3N} = \left(\frac{L}{\lambda_{th}(T)}\right)^{3N}$$

For convenience, define $\lambda_{th}(T) = \sqrt{\frac{2\pi\hbar^2}{mT}} \ll L$

thermal de Broglie wavelength

Final result: $Z_D = \left(\frac{mTL^2}{2\pi\hbar}\right)^{3N/2} = \left(\frac{L}{\lambda_{th}}\right)^{3N} = \left(\frac{V}{\lambda_{th}^3}\right)^N = Z_1^N$

Depends on volume V along with N and T

What about indist'able particles?

Can't be labelled $\rightarrow$ half as many micro-states for $N=2$

For $N=3$ (assuming $\vec{p}_i \neq \vec{p}_k$ for $i \neq k$)

single indist'able w_i $\longleftrightarrow$ $6=3!$ dist'able micro-states from labels

$\vec{p}_1$	A	A	B	B	C	C
$\vec{p}_2$	B	C	A	C	B	A
$\vec{p}_3$	C	B	C	A	A	B

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General result: $Z_I = \frac{1}{N!} Z_D = \frac{1}{N!} Z_1^N = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N = \frac{1}{N!}\left(\frac{mTL^2}{2\pi\hbar^2}\right)^{3N/2}$

Helmholtz free energy $F_I = -T \log Z_I$

$$= T\log(N!) - T\left(\frac{3N}{2}\right)\log\left(\frac{mTL^2}{2\pi\hbar^2}\right)$$

Derive $\langle E\rangle_I = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right) = -T^2\frac{\partial}{\partial T}\left(-\frac{3N}{2}\log T + T\text{-indep.}\right)$

$$= \frac{3NT}{2}$$

Sensible macroscopic relation
from microscopic dynamics ✓

Entropy is $S_I = \frac{\langle E\rangle - F}{T} = \frac{3N}{2} + \frac{3N}{2}\log\left(\frac{L^2}{\lambda_{th}^2}\right) - \underbrace{\log(N!)}_{N\log N - N}$

$$\approx \frac{5N}{2} + N\log\left(\frac{V}{N\lambda_{th}^3}\right)$$

Depends on volume
information from locations

$$\boxed{\begin{array}{l}\text{Dist'able case just drops } \log(N!) \\ F_D = \frac{-3NT}{2}\log\left(\frac{mTL^2}{2\pi\hbar^2}\right) \\ \langle E\rangle_D = \frac{3}{2}NT = \langle E\rangle_I \\ S_D = \frac{3}{2}N + N\log\left(\frac{V}{\lambda_{th}^3}\right)\end{array}}$$